博 士 論 文 内 容 の 要 旨

専攻名 物質工学

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1 論文題目（英文の場合は，和訳を付記すること）

Study on the new way to prepare the materials for lithium ion battery by using fluorine or chlorine trifluoride

フッ素または三フッ化塩素を用いたリチウム含有化合物の新規合成プロセスおよび表面修飾に関する研究

2 要 旨（和文 2,000 字程度又は英文 800 語程度にまとめること。）

Lithium ion batteries are used as the power sources for the electric vehicles and portable devices because of their lighter weight and higher energy/power densities than the other secondary batteries such as lead acid and nickel hydrogen batteries. Commercially provided lithium ion battery consists of the cathode containing ceramics active material like $LiCoO_2$, graphite anode and the electrolyte solution containing $LiPF_6$ as the supporting salt. In order to prepare higher performance lithium ion battery, it is required for Li^+ in it to have higher mobility through the total redox process. At least there may be three kinds of Li^+ transfer process in the lithium ion battery. One is the transfer of Li^+ in the electrode active materials, and the others are that in the electrolyte and that across the electrochemical reaction field near the surface of the active material. In this study, the Li^+ transfer in the electrolyte and across the surface of the active material have been focused. Using inorganic fluorine chemistry, the new process preparing $LiPF_6$ which may conduct high performances in the lithium ion batteries and the new technique of the surface modification to accelerate the Li^+ transfer during the electrochemical reaction have been investigated.

In chapter 1, the new process to prepare $LiPF_6$ as the material of the electrolyte for high performance lithium ion battery has been reported. Since the solubility of $LiPF_6$ into the organic solvents used for lithium ion batteries is higher than that of other

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compounds such as $LiBF_4$ and $LiClO_4$, the electrolyte solution containing $LiPF_6$ exhibits high electric conductivity. In addition, $LiPF_6$ is stable against the redox reaction in the lithium ion battery. The electrolyte solution containing $LiPF_6$, however, contains HF as an impurity. In fact, HF contamination degrades the performance of lithium ion batteries. Therefore, numerous efforts have been undertaken to develop a process by which highly pure $LiPF_6$ is obtainable. Several methods are used in industry. For example, LiF is dissolved into liquid anhydrous hydrogen fluoride (L-AHF) and PF_5 gas is supplied into this system. $LiPF_6$ is generated and precipitated as a crystal. Alternatively, LiF and PCl_3 are reacted in L-AHF to obtain the $LiPF_6$ crystal. Generally AHF is used as the medium for these methods (AHF method). However, HF can remain in the products produced using these methods. Although the amount of HF in the product is extremely small, its presence causes deliquescence of the products because HF gives hygroscopicity to the product and promotes the hydrolysis of $LiPF_6$ to form LiPOxFy and HF. The preparation of $LiPF_6$ without AHF can be addressed to solve this problem. Among them, the reaction among LiF, P, and F_2 is the simplest AHF-free method to prepare $LiPF_6$. It has been reported that pure lithium hexafluorophosphate ($LiPF_6$) was successfully prepared at room temperature (23 °C) by introducing fluorine gas into a reactor containing LiF and P at -196 °C in this chapter. The mass fractions of $LiPF_6$ and LiF in products prepared at 23 °C were 1.00 and 0.00, respectively, by means of XRD-Rietveld analysis. Namely, the prepared $LiPF_6$ was pure enough to be used as an electrolyte salt in lithium ion batteries. Highly pure $LiPF_6$ was obtained using this F_2 method: purer than that obtained using L-AHF method. However, with F_2 method, it is difficult to control the reaction because the exothermal reaction between P and F_2 proceeds vigorously. To maintain the temperature of the reaction system, for example, F_2 gas must be introduced into the system very slowly.

In chapter 2, the preparation process of $LiPF_6$ from Li, P and ClF_3 has been investigated instead of using F_2 gas as fluorinating reagent. No PF_3 gas was found in the product gases and solid products in this process. The PF_5 generated using the previous process must react with LiF in the presence of ClF_3 to generate $LiPF_6$. The reaction preparing $LiPF_6$ from LiF, P, and ClF_3 can take place even at 0 °C. Moreover, it can be promoted by increasing the reaction temperature. However, if the reaction temperature increases, impurities from the decomposition of $LiPF_6$ are generated,

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especially at temperatures higher than 100 °C. For the preparation of $LiPF_6$, the reaction of LiF + P + ClF_3 presents several benefits, such as low reaction temperature and short reaction time, that are absent from the LiF + P + F_2 reaction. Separating LiF from the product is extremely simple because LiF is insoluble to organic solvents such as propylene carbonate, THF and others, while $LiPF_6$ (also $LiPO_2F_2$) is soluble to those. In fact, the electrolyte solution was prepared by dissolving the products into PC+DME (1:1 in vol.) and filtering it to remove insoluble species such as LiF. The results of charge/discharge tests with these electrolyte solutions and consideration of the amounts of impurities and yields show that the optimal conditions to prepare $LiPF_6$ using the method here are 25 °C reaction temperature and 5 h reaction time.

In chapter 3, the new technique of the surface fluorination of $LiFePO_4$, the cathode active material. The electrochemical properties and thermal stability of carbon coated $LiFePO_4$ cathode were improved by the surface fluorination using NF_3 gas at a pressure less than 6.67 kPa at 25 °C. Especially, in case of F1-$LiFePO_4$, the discharge capacity was about 10% higher than that of untreated $LiFePO_4$. Also it indicated the lowest resistance (R_{ct} = 35.55 Ω) and largest exchange current density (i_0 = 0.72 mA) from the EIS results. However, in case of F_2-$LiFePO_4$, the electrochemical properties were negatively affected by the formation of some resistive fluoride films. In terms of thermal stability, the decomposition temperature (222.0 °C) of F1-$LiFePO_4$ was 14 °C higher than that of untreated $LiFePO_4$. Therefore, the surface fluorination led to the improvement of electrochemical properties and thermal stability of $LiFePO_4$ as a promising cathode in high power lithium-ion cells for HEVs.

Consequently it has been reported that the new processes to prepare the materials of lithium ion batteries by using F_2, ClF_3 and NF_3. The information shown in this paper must contribute to preparing the high performance lithium ion cells.